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Bescheinigung

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Attestation

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#2

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The attached documents are exact copies of the European patent application described on the following page, as originally filed.

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Patentanmeldung Nr. **Patent application No.** **Demande de brevet n°**

99307065.5

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Sheet 2 of the certificate
Page 2 de l'attestation

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MIXING DEVICE

The present invention concerns catalytic partial oxidation of a fuel. In particular the present invention relates to a mixing device suitable for mixing a gaseous stream comprising a fuel and a gaseous oxidant, to a reactor for the partial oxidation of the fuel comprising such a mixing device, and to a catalytic partial oxidation process using such a mixing device.

Partial oxidation of a fuel, in particular hydrocarbons, in the presence of a catalyst is an attractive route for the preparation of mixtures of carbon monoxide and hydrogen, normally referred to as synthesis gas. The partial oxidation of paraffinic hydrocarbons is an exothermic reaction represented by the equation:

$$C_nH_{2n+2} + n/2\ O_2 \rightarrow n\ CO + (n+1)\ H_2$$

There is literature in abundance on the catalysts and the process conditions for the catalytic partial oxidation of gaseous hydrocarbons, in particular methane. Reference is made, for instance, to EP-A-303 438, US-A-5,149,464, and International patent application WO 92/11199.

Since the catalytic partial oxidation reaction proceeds at very short contact times (in the order of tens of milliseconds), it is necessary that the reactants are well-mixed when brought into contact with the catalyst. Otherwise, the reaction will proceed at an undesirable stoichiometry and the desired product selectivity will not be obtained.

contacted can be quantified by measuring the time-averaged values for X_{HC}/X_{O2} at different locations within the plane perpendicular to the flow direction of the mixture at that certain distance.

Mixers should be such that a low time-averaged value for γ is achieved at a short distance from the initial point of contact or within a short time after initial contact between the reactants. Preferably, a value for γ below 0.1, more preferably below 0.05, is achieved within a residence time of 15 milliseconds.

It is not only important that the time-averaged values for γ are low, but also that the flow has a high stability, i.e. that the fluctuations in the ratio X_{HC}/X_{O2} at a single location and at short time scales are small. Reference to short time scales is to time scales in the order of the thermal response time of the upstream surface of the catalyst bed, typically in the order of tens of milliseconds. The flow stability can be quantified by the measure δ, which is the quotient of the root mean square and the average of the values of the ratio X_{HC}/X_{O2} measured several times at a single location, each measurement with a short sampling time. Thus δ is defined as:

$$\delta = \frac{\sqrt{\dfrac{\sum_{i=1}^{n}\left((X_{HC}/X_{O2})_i-(X_{HC}/X_{O2})_{av}\right)^2}{(n-1)}}}{(X_{HC}/X_{O2})_{av}}$$

wherein n is the number of measurements of X_{HC}/X_{O2} at a single location, each measurement carried out with a short sampling time. Ideally, the value for δ is of the same order of magnitude or smaller than the time-averaged value for γ.

Surprisingly it has been found that a very high mixing rate, at a high flow stability can be achieved by using a novel mixing device wherein a gaseous stream containing the hydrocarbonaceous fuel is tangentially injected perpendicular to an axially-injected, oxygen-containing stream, without the occurrence of impingement. Accordingly, the mixing device of the present invention comprises a cylindrical mixing chamber, means for injecting a gaseous stream comprising a fuel tangentially along the inner surface of the wall of the mixing chamber, and means for injecting a gaseous stream of oxidant axially along the central longitudinal axis of the mixing chamber, wherein the diameter of the mixing chamber and the dimensions and location of the means for injecting the fuel and the oxidant are such that, during normal operation, the tangentially injected stream comprising the fuel forms a wall jet around the axially injected stream of the oxidant without impinging upon the axially injected stream.

The mixing device of the present invention is particularly suitable for mixing a hydrocarbonaceous fuel and an oxygen-containing gas, prior to the partial oxidation of the hydrocarbonaceous fuel. Accordingly, the present invention further relates to a reactor comprising a mixing device as hereinbefore defined and a partial oxidation zone.

The partial oxidation zone may be any partial oxidation zone known in the art, such as a non-catalytic partial oxidation zone, an autothermal reforming zone or a catalytic partial oxidation zone, preferably a catalytic partial oxidation zone.

The mixing device and the reactor of the invention will now be illustrated in a non-limiting manner with reference to the schematic Figures 1 to 4.

mixing chamber 2 has an inner diameter 14. Reference herein to the diameter 12 of the stream 6 of oxidant is to the diameter at the outlet opening 8 of the means for injecting the stream 6. Reference to the width 13 of the fuel-comprising stream 3 is to the width in the perpendicular plane wherein the fuel-comprising stream 3 is injected. A perpendicular plane refers to a plane perpendicular to the longitudinal axis of the cylindrical mixing chamber 2.

Figure 3 shows a preferred embodiment of the mixing device 1 of the present invention wherein the means for injecting a stream of fuel-comprising gas comprise two axially placed apart inlet tubes 4.

Figure 4 shows a reactor 15 according to an embodiment of the present invention. The reactor 15 comprises a mixing device 1 and a catalyst bed 16 in the form of a piece of ceramic foam. The mixing device 1 comprises a mixing chamber 2, means for tangentially injecting a stream 3 of fuel-comprising gas comprising two sets of two axially spaced apart inlet tubes 4, means for injecting an oxidant comprising a single inlet tube 7, and a diffuser 17 with an insert 18. The inlet tubes 4 of the means for injecting the fuel each have an inner diameter of 5 mm, the inlet tube 7 of the means for injecting the oxidant has an inner diameter of 8 mm. The height and the inner diameter 14 of the mixing chamber 2 are 26.5 and 24 mm, respectively.

It is a requirement of the mixing device of the present invention that the inner diameter 14 of the mixing chamber 2 and the dimensions and location of the means 4,5,7,8 for injecting the fuel and the oxidant are such that, during normal operation, the tangentially injected stream 3 comprising the fuel forms a wall jet around the axially injected stream 6 of the oxidant without impinging upon the axially injected stream 6.

arranged in a perpendicular plane at regular intervals along the circumference of the cylindrical mixing chamber 2, for example two opposite, diametrical openings as shown in Figure 1.

The means for injecting the stream 6 of oxidant may be any means suitable for forming a gas jet along the central longitudinal axis of the mixing chamber 2. Preferably, the oxidant is injected into the mixing chamber 2 through a single opening. Examples of a suitable means for injecting are a nozzle, an inlet opening or the outlet opening of an inlet tube.

The opening(s) through which the stream 6 of the oxidant is injected into the mixing chamber 2 is (are) located at the same level or near the level of the top cover 10, preferably at the level of the top cover 10. The stream 3 of the fuel-comprising gas is preferably injected into the mixing chamber 2 at the same level or just downstream of the level at which the stream 6 of oxidant is injected.

It has been found that the mixing rate can be further improved by injecting a stream 3 of the fuel-comprising gas having a width d_{fuel} and a major axis in the direction of the longitudinal axis of the mixing chamber 2 which is greater than its width d_{fuel}. Thus, a wall jet is formed over a greater length of the cylindrical side wall 11 of the mixing chamber 2. This can be achieved by means of an opening having an oval shape, for example a slit, with the major axis parallel to the longitudinal axis of the mixing chamber 2 or by means of two or more axially placed apart openings, such as shown in Figures 3 and 4.

The mixing device of the present invention is particularly suitable for operating at higher Re numbers, i.e. typically above 10^4. Reference herein to Re numbers

zirconia and mixtures thereof, and metals. High-alloy, alumina-containing steel, such as fecralloy-type materials are particularly suitable metals. The catalyst may comprise the catalytically active metal in any suitable amount to achieve the required level of activity. Typically, the catalyst comprises the active metal in an amount in the range of from 0.01 to 20% by weight, preferably from 0.02 to 10% by weight, more preferably from 0.1 to 7.5% by weight. In addition to the catalytically active material, the catalyst may comprise a promoter or performance-enhancing compound. Suitable promoters are known in the art.

Preferably, the fuel-comprising gas is a gaseous hydrocarbonaceous fuel. Alternatively, the fuel-comprising gas is an inert carrier gas comprising droplets of a liquid hydrocarbonaceous fuel, for example naphtha, kerosene or synthetic gas oil.

The hydrocarbonaceous fuel is in the gaseous phase when brought into contact with the catalyst during operation. The fuel may contain compounds that are liquid and/or compounds that are gaseous under standard conditions of temperature and pressure (i.e. at 0 °C and 1 atm.).

Preferably, the hydrocarbonaceous fuel comprises methane, natural gas, associated gas or other sources of light hydrocarbons. In this respect, the term "light hydrocarbons" is a reference to hydrocarbons having from 1 to 5 carbon atoms.

The hydrocarbonaceous fuel may comprise oxygenates (being gaseous and/or being liquid under standard condition of temperature and pressure). Oxygenates to be used as (part of) the fuel in the process according to the present invention are defined as molecules containing apart from carbon and hydrogen atoms at least 1 oxygen atom which is linked to either one or two carbon atoms or

For applications on a commercial scale, elevated pressures, that is pressures significantly above atmospheric pressure are most suitably applied in the process of the present invention. The process is preferably operated at pressures in the range of from 2 to 150 bar (absolute). More preferably, the process is operated at pressures in the range of from 2 to 100 bar (absolute), especially from 5 to 50 bar (absolute).

Under the preferred conditions of high pressure prevailing in processes operated on a commercial scale, the feed mixture is preferably contacted with the catalyst bed at a temperature in the range of from 750 to 1400 °C, more preferably of from 850 to 1350 °C, even more preferably of from 900 to 1300 °C. Reference herein to temperature is to the temperature of the gas leaving the catalyst.

The feed mixture may be provided during the operation of the process at any suitable space velocity. It is an advantage of the process of the present invention that very high gas space velocities can be achieved. Thus, gas space velocities for the process (expressed in normal litres of gas per kilogram of catalyst per hour, wherein normal litres refers to litres under STP conditions, i.e. 0 °C and 1 atm.) are in the range of from 20,000 to 100,000,000 Nl/kg/h, more preferably in the range of from 50,000 to 50,000,000 Nl/kg/h. Space velocities in the range of from 500,000 to 30,000,000 Nl/kg/h are particularly suitable for use in the process.

<u>EXAMPLE</u>

In the reactor (15) as shown in Figure 4, a stream (6) of 4.4 grams per second of oxygen (density is 1.7) having a temperature of 22 °C is axially injected through the outlet opening (8) of inlet tube (7) and a stream of 4.7 grams per second of natural gas (density is

C L A I M S

1. A mixing device for mixing a gaseous stream comprising a fuel and a gaseous oxidant, which mixing device comprises a cylindrical mixing chamber, means for injecting the gaseous stream comprising the fuel tangentially along the inner surface of the wall of the mixing chamber, and means for injecting a stream of the oxidant axially along the central longitudinal axis of the mixing chamber, wherein the diameter of the mixing chamber and the dimensions and location of the means for injecting the fuel and the oxidant are such that, during normal operation, the tangentially injected stream comprising the fuel forms a wall jet around the axially injected stream of the oxidant without impinging upon the axially injected stream.

2. A mixing device according to claim 1, wherein, during normal operation,

$d_{ox} < d_{mix} - 3 . d_{fuel}$

wherein:

d_{ox} is the diameter of the stream of the oxidant at the point where the stream of the oxidant is injected;

d_{mix} is the diameter of the mixing chamber; and

d_{fuel} is the width of the stream comprising the fuel in a perpendicular plane wherein the stream comprising the fuel is injected.

3. A mixing device according to claim 1 or 2, wherein the means for injecting the stream comprising the fuel comprise at least two openings arranged in a perpendicular plane at regular intervals along the circumference of the cylindrical mixing chamber.

pressure in the range of from 2 to 150 bar (absolute), preferably of from 5 to 50 bar (absolute).

14. A process according to any of claims 9 to 13, wherein the feed mixture is contacted with the catalyst at a gas hourly space velocity of from 20,000 to 100,000,000 Nl/kg/h, preferably of from 50,000 to 50,000,000 Nl/kg/h, more preferably of from 500,000 to 30,000,000 Nl/kg/h.

15. A process according to any of claims 9 to 13, wherein the feed mixture is contacted with the catalyst at a temperature of from 750 to 1400 °C, preferably of from 850 to 1350 °C, more preferably of from 900 to 1300 °C.

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A B S T R A C T

MIXING DEVICE

The invention relates to a mixing device (1) for mixing a gaseous stream comprising a fuel and a gaseous oxidant, which mixing device (1) comprises a cylindrical mixing chamber (2), means (4,5) for injecting a gaseous stream comprising the fuel tangentially along the inner surface of the wall of the mixing chamber (2), and means (7,8) for injecting a stream (6) of the oxidant axially along the central longitudinal axis of the mixing chamber (2), wherein the diameter (14) of the mixing chamber (2) and the dimensions and location of the means (4,5,7,8) for injecting the fuel and the oxidant are such that, during normal operation, the tangentially injected stream comprising the fuel forms a wall jet around the axially injected stream (6) of the oxidant without impinging upon the axially injected stream (6). The invention further relates to a reactor for the partial oxidation of a hydrocarbonaceous fuel comprising the mixing device and to a process for the catalytic partial oxidation of a hydrocarbonaceous fuel using the mixing device.

(Figure 1)

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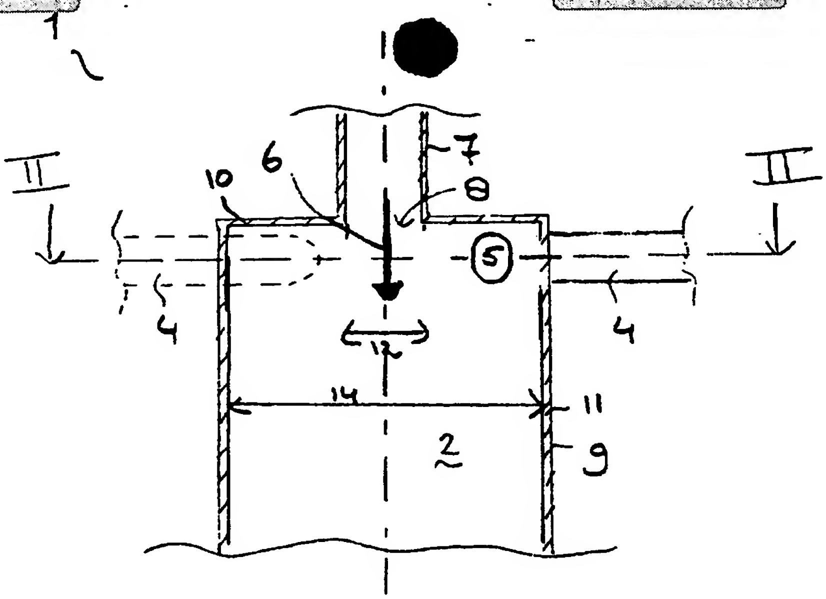

Fig 1

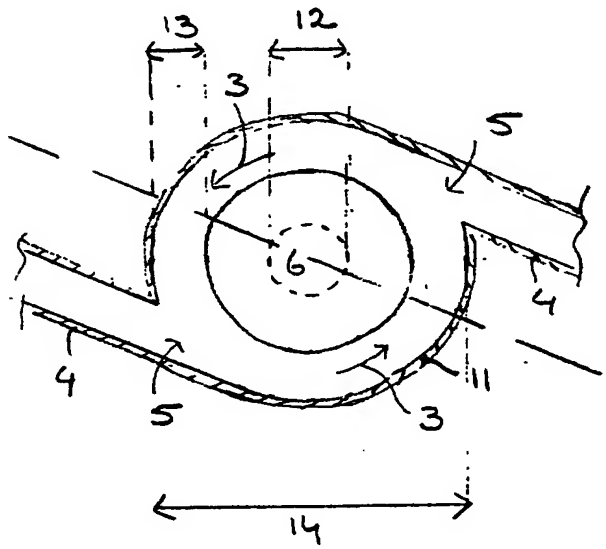

Fig 2

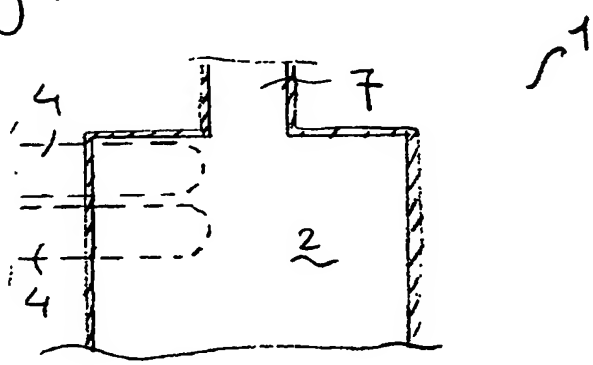

Fig 3